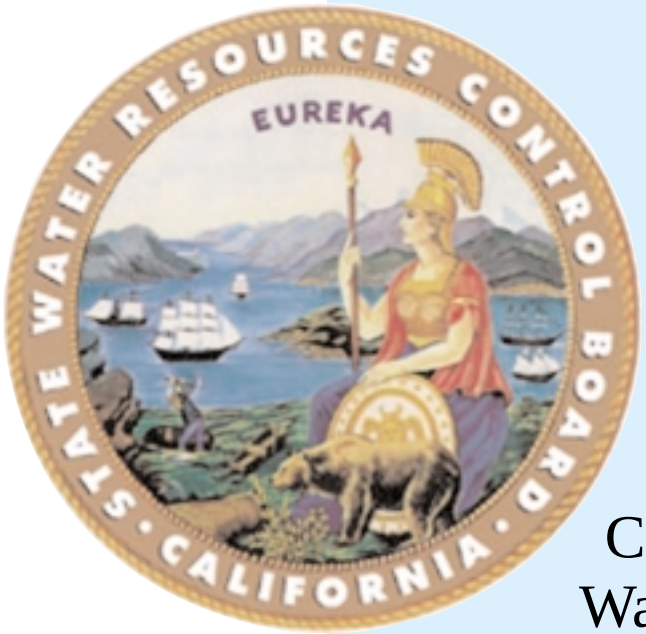
UCRL-AR-145380

Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate:

Subsurface Fate and Transport of Gasoline Containing Ethanol



Report to the California State Water Resources Control Board

Editors

David W. Rice

Rosanne T. Depue

October 2001

Table of Contents

Executive Summary

This document describes continuing research into possible impacts on ground water resources that may be associated with increased use of ethanol in gasoline. Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999, calling for the removal of methyl tertiary butyl ether (MtBE) from gasoline at the earliest possible date but no later than December 31, 2002. In December, 1999, a report entitled *The Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate* summarized the results of a screening analysis performed in fulfillment of the requirements of the Executive Order. As a result of this report, the California Environmental Policy Council found that the impacts associated with the use of ethanol will be significantly less and more manageable than those associated with the continued use of MtBE, but that further research was warranted.

The ongoing research conducted to meet the California Environmental Policy Council's requirements involved laboratory studies using field materials collected from a variety of fuel release sites, including a site where bulk ethanol was released. These laboratory studies examined the:

- Behavior of ethanol-containing gasoline (gasohol) as it infiltrates through the unsaturated zone.
- Biodegradation kinetics of the gasoline components benzene, toluene, ethylbenzene, and xylenes (BTEX) in the presence of ethanol.
- Ethanol-related changes in subsurface bacterial populations (microbial ecology) that may influence the biodegradation rates of gasoline components.

In addition to laboratory studies, further ground water impact modeling was performed and ethanol chemical analysis and sample handling methods were evaluated.

Research Findings

- During a gasohol spill, a significant fraction of the ethanol dissolves into the residual soil moisture normally present in the unsaturated zone above the water table. The gasoline components without the ethanol continue to migrate to the water table and form a pool of floating fuel hydrocarbons. Depending on the volume of the spill, the ethanol in the unsaturated zone could then drain slowly into the floating hydrocarbon pool, creating a central localized region with a high ethanol concentration. The remainder of the fuel hydrocarbons floating on the water table behave much the same as a spill of gasoline without ethanol.
- The fraction of ethanol retained in the unsaturated zone depends greatly on the volume of soil impacted by the release, the water content of the soil, and the rate at which gasoline infiltrates through the subsurface.
- Ethanol was typically degraded before BTEX compounds. The preferential degradation of ethanol and the accompanying depletion of oxygen and other electron acceptors suggest that ethanol could impede the natural attenuation of BTEX plumes. The rate of

natural microbial degradation of ethanol and gasoline fuel hydrocarbons is related to the abundance of electron acceptors such as oxygen. When oxygen is depleted (anaerobic conditions), some microbes use electron acceptors such as nitrate, sulfate, and carbon dioxide. BTEX biodegradation rates under anaerobic conditions are slower than when oxygen is present (aerobic conditions). This is particularly important because benzene, a known human carcinogen, is the most recalcitrant of the BTEX compounds under anaerobic conditions.

- Of the anaerobic electron-accepting conditions tested, denitrifying conditions (i.e., where nitrate is the primary electron acceptor) were clearly the most supportive of anaerobic BTEX degradation.
- Ethanol had a variable effect on toluene degradation. In some cases, ethanol retarded toluene degradation, but it occasionally enhanced toluene degradation. The variable effect of ethanol on toluene degradation was a function of electron-accepting conditions and the bacterial community present. Enhancement of toluene degradation by ethanol when electron acceptors are supplied in excess may be attributable to the fortuitous growth of toluene-degrading bacteria during ethanol degradation.
- BTEX and ethanol were typically, but not always, degraded more rapidly during experiments that used aquifer soil previously contaminated with fuel hydrocarbons.
- The results for the new DNA-based method developed for this study suggest that the relationship between microbial ecology and hydrocarbon degradation activity in gasohol-contaminated aquifers can be complex and site-specific.
- Ethanol often decreased the relative populations of anaerobic hydrocarbon-degrading bacteria (i.e., relative to total bacteria). This indicates that ethanol, which is generally more degradable than BTEX compounds under anaerobic conditions, can disproportionately enhance the growth of bacteria that are not anaerobic hydrocarbon degraders. This didn't have a notable effect on hydrocarbon degradation activity in short-term laboratory experiments, but could potentially hinder the anaerobic hydrocarbon degradation in aquifers.
- Modeling results indicate a possible four-fold decrease in the mean benzene biodegradation rate as a consequence of ethanol biodegradation and associated electron acceptor depletion. This could potentially increase benzene plume lengths by a factor of roughly 2.5. This is a conservative modeling scenario that treats the ethanol and benzene source terms as simple injection processes at a point; the impact of ethanol on the fuel hydrocarbons floating on top of the water table is not taken into account.

The evaluation of ethanol sampling and chemical analysis methods found that:

- Acidification of ground water samples followed by refrigeration adequately preserves ethanol in ground water samples for longer than two weeks. Ethanol in samples can be easily degraded, so care should be taken to preserve samples as quickly as possible after collection. Refrigeration without preservation does little better than no preservation at all.

- It is reasonable to expect that analytical laboratories can achieve reporting limits of 50–500 *ppb* for ethanol in clean ground water. Reporting limits will be increased in the presence of interferences caused by other gasoline components.
- There is a need for improved characterization of methane and volatile fatty acids at ethanol release sites. Bulk fuel ethanol spills and some gasohol releases could pose an explosion risk when site-specific conditions favor extensive methanogenesis and methane accumulation. In addition, ethanol-derived acetate and other volatile fatty acids could cause a decrease in pH (thus hindering biodegradation processes) and create taste and odor problems. Therefore, site characterization protocols should include methane and volatile fatty acid analyses near the release area.

Further Research Recommendations

- Additional laboratory studies are needed to better quantify the functional relationships that control the retention of ethanol in the unsaturated zone. These studies should examine the retention of ethanol as a function of soil type, moisture content, and spill rate.
- Improved modeling is needed to integrate and better represent ethanol degradation kinetics and the complex behavior of gasoline fuel hydrocarbons in the presence of ethanol. A spill of gasohol into the subsurface should not be modeled as a pool of gasoline with constant composition throughout. This modeling should include the dissolution of ethanol into the water in the unsaturated zone as well as the resulting impacts to the floating fuel hydrocarbons on the water table.

  The biodegradation component of the model should, to the extent possible, integrate the negative effects of ethanol on BTEX degradation (e.g., electron acceptor depletion) with potential positive effects (e.g., enhanced growth of BTEX-degrading bacteria).
- A controlled field release of gasohol and additional study of known gasohol release sites should be conducted. One major concern is that ethanol could increase the distance that BTEX compounds migrate before being attenuated to acceptable concentrations by natural processes. Nevertheless, there is considerable uncertainty regarding the magnitude and significance of this potential impact. Therefore, field-scale studies should be conducted to quantify the effect of ethanol on plume length. Such studies could include controlled-release (field) experiments and statistical analyses of leaking underground fuel tank site data with and without ethanol. Controlled-release studies should be multidisciplinary and could benefit from incorporation of the microbial ecology technique developed as part of the ongoing research performed to date.

Implications for Cleanup of Gasoline Releases

- Cleanup strategies should be considered that stimulate biodegradation under anaerobic conditions. The most common engineered bioremediation approaches used for BTEX cleanup are aerobic, introducing oxygen to stimulate biodegradation. Applying sufficient oxygen to meet the high oxygen demand exerted by ethanol will likely be technically difficult and prohibitively expensive. The lack of field experience with enhanced

anaerobic bioremediation approaches for BTEX contamination will require the refinement and demonstration of suitable approaches. These could include the addition of nitrate to increase the electron acceptor pool (in a manner that does not create toxicity or clogging problems).